THE ELECTRICAL CONDUCTIVITY OF SOLID CHLORINE AND BROMINE TRIFLUORIDES

Madeline S. Toy and William A. Cannon

Astropower Laboratory of Douglas Aircraft Co., Inc.
Newport Beach, California

Introduction

The interest in conductivity measurements on fluorinated inorganic compounds at cryogenic temperatures lies in the ability of these compounds to form ions for possible synthesis of potential solid oxidizers. In the present study we are concerned with the conductivity measurements on solid chlorine and bromine trifluorides to determine their electrical conductivities and their bearing on structural problems. Specific conductivities of $< 10^{-6}$ at 0°C(1) and 10^{-9} $ohm^{-1}cm^{-1}$(2) have been reported for chlorine trifluoride and 8.0×10^{-3} $ohm^{-1}cm^{-1}$ at 25°C(1) for bromine trifluoride. In this work a conductivity cell has been developed for measurement of fluorine-containing oxidizers at cryogenic temperatures. The variations of conductivity with temperature of chlorine trifluoride have been measured from -11.3°C (b.p.) to -130°C (well below m.p., -83°C) and of bromine trifluoride from +80°C to -196°C (m.p., 8.8°C). Possible mechanisms are discussed.

Experimental

Materials. - Chlorine and bromine trifluorides were obtained from the Matheson Co. Chlorine trifluoride was purified by passing the vapor through a sodium fluoride scrubber to remove possible hydrogen fluoride impurity and then fractionally distilled. Bromine trifluoride was used without additional purification.

Conductivity Measurements. - Cell resistance measurements were made with a General type 1650-A Impedance Bridge. It is equipped with an internal, 1000-cycle signal source and tuned null detector. For more sensitive balance at high resistances, a Hewlett Packard 400L vacuum tube voltmeter is used as an external null detector.

The conductivity cell is modified from a conventional type. It is made of borosilicate glass, which resists the attack of anhydrous chlorine and bromine trifluorides, and is equipped with two smooth platinum electrodes to minimize electrode corrosive effects. These electrodes are approximately 12 x 25 mm in size held 1.5 mm apart with borosilicate glass spacers. The arrangement of electrodes and leads is shown in Figure 1. An internal thermocouple well leads from the top of the cell to a point near the electrodes and contains a copper-constatan thermocouple. The cell constant is determined by measuring the cell resistance while the cell is filled with 0.001 N KCl solution at 25°C (cell constant = specific conductivity x observed resistance, where specific conductivity of 0.001 N KCl at 25°C = 0.00014695 $ohm^{-1}cm^{-1}$). The change in cell constant due to changes in cell and electrode dimensions has been calculated to be insignificant to as low as -195°C and is therefore ignored in this work.

The possibility of imperfect contact of the solid with the electrode does not seem to be a problem in view of the uniformity of the curves and reproducibility as indicated below.

Results and Discussion

Conductivity Versus Temperature of Chlorine Trifluoride. - The conductivity of chlorine trifluoride has been measured over the temperature range from near the boiling point (+11.3°C) to -130°C. Figures 2 and 3 are plots of the conductivity as a function of temperature as the sample of chlorine trifluoride is cooled from the boiling point at a rate of approximately 2 to 3°C per minute. The conductivity increases slightly as the sample is cooled and displays a small maximum before the freezing point (m.p. -83°C) is reached. Below the freezing point the conductivity increases rapidly to a sharp maximum. The temperature versus conductivity plot (Figure 2) for a sample purified by low temperature fractionation[3] no longer has the small maximum occurring just above the freezing point and the maximum peak has been broadened and displaced to a lower temperature. It was thought that the broadening of the peak may reflect the presence of trace carbon halides or chlorine impurities which might have been introduced through reaction of chlorine trifluoride with Kel-F grease used on the stopcocks in the distillation apparatus. Therefore, the distillation manifold was rebuilt using stainless steel needle valves in place of stopcocks. No grease was used in any part of the distillation equipment or manifold (Figure 4). When the experiment was repeated the same general trend was noted, i.e., the disappearance of the small discontinuity above the freezing point, and the displacement to lower temperature and broadening of the conductivity maximum. The results are plotted in Figure 3. It is likely that the necessarily long residence time in glass (ca. 24 hr.) required for the distillation results in pickup of ionic impurities. This could account for the enhanved conductivity in both the solid and liquid after low temperature fractionation.

Solid chlorine trifluoride has a negative temperature coefficient for the conductivity within a narrow temperature range below the freezing point. This negative temperature effect is likely due to a decrease in stability of one or both of the postulated ionic species (ClF_2^+ and ClF_4^-) with increasing temperature rather than electronic conduction. Indirect evidence of the existence of ClF_2^+ cation is supported by the isolation of the compounds ClF_2AsF_6 and ClF_2SbF_6 by Seel and Detmer[4] and ClF_2BrF_4 by Selig and Shamir.[5] An alternative possibility is that the solid is polycrystalline and that conduction depends on grain boundary surface. Such a solid would be molecular and conduction would occur in surface and grain boundary films where ClF_3 is slightly ionized. The portion of ions in such absorbed films is greater than in the bulk liquid since ionization would favor absorption on the possibly dipolar solid. The decrease in conductivity with increasing temperature is then due to a decrease in inner surface.

Conductivity Versus Temperature of Bromine Trifluoride. - The conductivity of bromine trifluoride has been measured over a range of 80 to -196°C (Figure 5). There is little variation of conductivity with temperature in the liquid state; the liquid has a tendency to supercool. The value of specific conductivity at 25°C is 5.03×10^{-3} ohm^{-1} cm^{-1}; literature value is 8×10^{-3} ohm^{-1} cm^{-1}.[1] The ions accounting for the conductivity are probably BrF_2^+ and BrF_4^-. Woolf and Emeleus[6] reported the existence of the ionic equilibrium

$$2\ BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

in liquid bromine trifluoride by the isolation of compounds BrF_2SbF_6 and $(BrF_2)_2SnF_6$ for BrF_2^+ cation and $KBrF_4$, $AgBrF_4$ and $Ba(BrF_2)_2$ for BrF_4^- anion.

Conductivity of solid bromine trifluoride decreased rapidly with temperature leading to a marked discontinuity around the melting point (+8.8°C). Another discontinuity is observed at ca. -20°C (Figure 5). There are two curves with different slopes, a higher temperature portion and a lower temperature portion. This is similar to the behavior of AgCl, AgBr, TlCl and TlBr as described by Lehfeldt.[7]

This suggests that solid bromine trifluoride may have an ionic lattice of BrF_2^+ and BrF_4^- ions and exhibit electrolytic conduction as these salts. Phosphorous pentachloride, which conducts to a small extent in the solid, has been shown to possess a lattice of PCl_4^+ and PCl_6^- ions. Electrolytic conduction is expressed as the exponential

$$\sigma = \sigma_o e^{-Q/kT} \qquad (1)$$

where σ_o is a constant that can be expressed in terms of mobilities, and Q is the activitation energy.[9] For the solid BrF_3 curve shown in Figure 5, it is to be expected that

$$\sigma = \sigma_o e^{-Q_1/kT} + \sigma_o' e^{-Q_2/kT} \qquad (2)$$

since two processes are operating. The activation energy Q_1 for the lower temperature process (between -20 and -196°C) is of the order of 3.81 Kcal/g mole, or one-eighth the value of Q_2, 29.8 Kcal/g mole (between +8.8° to -20°C), whereas σ_o (2.13×10^{-11} $ohm^{-1}cm^{-1}$) is many orders of magnitude greater than σ_o' (1.73×10^{-29} $ohm^{-1}cm^{-1}$).

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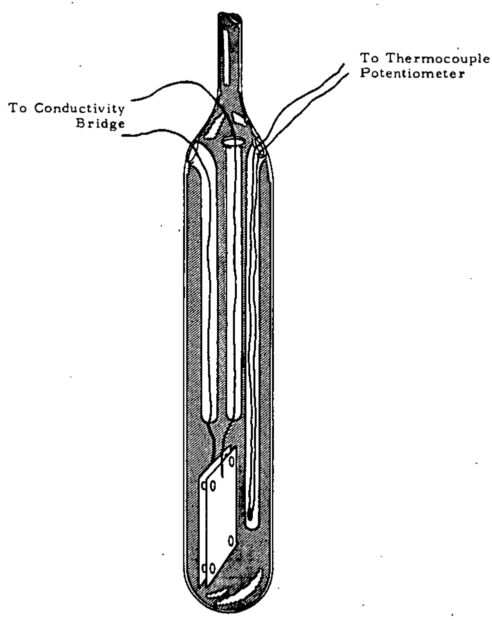

Figure 1. Conductivity Cell

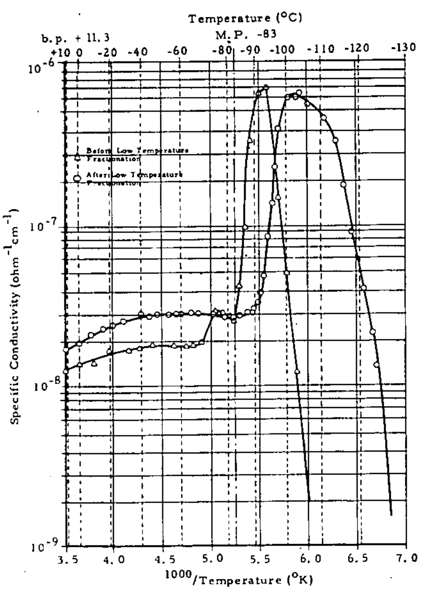

Figure 2. Conductivity of Chlorine Trifluoride as a Function of Temperature (I)

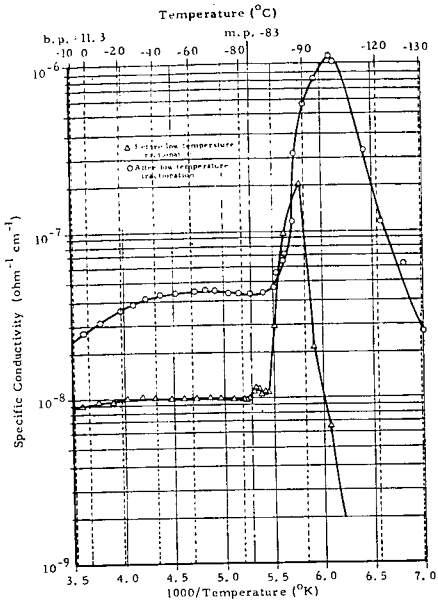

Figure 3. Conductivity of Chlorine Trifluoride as a Function of Temperature (II)

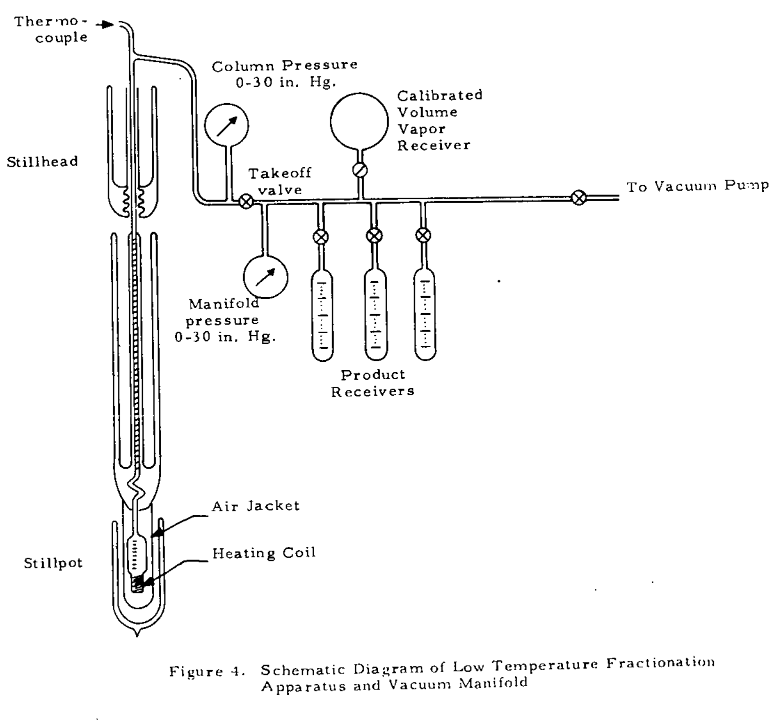

Figure 4. Schematic Diagram of Low Temperature Fractionation Apparatus and Vacuum Manifold

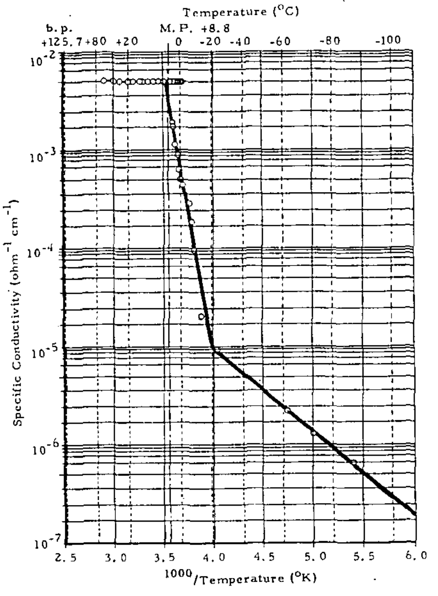

Figure 5. Conductivity of Bromine Trifluoride as Function of Temperature